

Spotlights on Recent JACS Publications

■ SIDE CHAINS IMPART SEMICRYSTALLINITY TO CONJUGATED POLYMERS

Semiconductors based on π -conjugated polymers are more amenable to solution processing than their inorganic counterparts and have the potential for applications in low-cost, large-area printed electronics. Researchers have found that by strategically modifying polymers with side chains, they can tailor certain properties—such as molecular packing and thin-film morphology—which in turn can affect the performance of device materials. Fluoroalkyl chains have several unique properties, such as hydrophobicity, rigidity, thermal stability, chemical and oxidative resistance, and the ability to self-organize. Yet the use of fluoroalkyl chains in organic semiconductors has not been investigated extensively.

Now, researchers led by Kilwon Cho and Yun-Hi Kim report a new semiconducting polymer with semifluoroalkyl side chains that is air-stable and exhibits superior electron mobility of up to $6.50 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (DOI: [10.1021/jacs.5b10445](https://doi.org/10.1021/jacs.5b10445)). The team modifies a naphthalene diimide-based conjugated polymer and finds the polymer with semifluoroalkyl side chains forms a superstructure composed of backbone crystals and side-chain crystals, resulting in a high degree of semicrystalline order. This phenomenon is attributed to the strong self-organization of the side chains and facilitates charge transport in organic semiconductors. The result sheds new light on optimizing electrical properties of high-mobility semiconducting polymers for field-effect transistor devices.

Christine Herman, Ph.D.

■ SURFACE LIGANDS FACILITATE METAL NANOCUSTER CATALYSIS

Metal nanoparticles' large surface areas have positioned them as prime choices for heterogeneous catalysts. For these applications, monodisperse nanoparticles are typically synthesized by colloidal chemistry using surface stabilizing agents. Stabilizing ligands that linger on the surface have generally been thought to “poison” catalysis, hindering reactions' forward progress. Now, Nanfeng Zheng, Quan-Ming Wang, and their co-workers show in a new study that surface ligands may in fact do just the opposite, with dramatically less efficient catalysis in their absence (DOI: [10.1021/jacs.5b12730](https://doi.org/10.1021/jacs.5b12730)).

To test the role of these ligands in catalysis, the researchers need to be able to easily strip the surface ligands from the nanoparticles without damaging the hosts. They find that intermetallic 62-metal-atom $\text{Au}_{34}\text{Ag}_{28}$ clusters allow easy removal of the phenylalkynyl ligands under mild thermal conditions while preserving the metal framework. The researchers compare the catalytic ability of treated and untreated nanoparticles in the hydrolytic oxidation of organosilanes to silanols. Nanoparticles exposed to thermal treatment scarcely catalyze the reaction, while untreated nanoparticles catalyze the conversion efficiently. The authors suggest that, rather than hindering catalysis, some surface ligands may in fact promote it.

Christen Brownlee

■ CAPTURED: ELUSIVE SILACYCLOBUTANONE AND 1-SILAKETENE

Carbonyl compounds play a central role in organic chemistry because of the versatile reactivity of the $\text{C}=\text{O}$ double bond that makes up this functional group. On the other hand, silanones, the silicon congeners of carbonyl compounds, are often too reactive to even be observed, and only a handful of these compounds have so far been prepared using ligand stabilization.

Now, Antoine Baceiredo, Tsuyoshi Kato, and co-workers have isolated and fully characterized a first-of-its-kind silacyclobutanone that is stabilized by an intramolecular donor (DOI: [10.1021/jacs.6b00631](https://doi.org/10.1021/jacs.6b00631)). Interestingly, at room temperature, the product can undergo $[2 + 2]$ -cycloreversion to yield a 1-silaketene complex stabilized by an N-heterocyclic carbene ligand.

This research adds to the short list of existing silanones and also presents an expandable strategy to access and transform reactive organosilicon compounds. More importantly, in the context of the renaissance of main group chemistry, these results will aid the better understanding and in-depth exploration of silicon in organic chemistry, and possibly also in synthetic applications.

Xin Su, Ph.D.

■ SELF-ASSEMBLY THAT WORKS LIKE BUILDING BLOCKS

Increasingly, nanomaterial assembly resembles building with toy blocks. Researchers choose the components and design nanomaterial synthesis so that the “blocks” end up in the right spots. Just as a limited number of blocks cannot yield very interesting creations, researchers seek to expand the number of molecular pieces at their disposal to create ever more interesting and useful materials. But these complex systems, which can contain hundreds of distinct pieces, are often difficult to program and control.

This Perspective discusses how theory can help researchers design and assemble such complicated multicomponent nanostructures. William Jacobs and Daan Frenkel examine the open challenges in predicting and controlling self-assembly of these systems with “addressable complexity”, focusing on the prediction of kinetic pathways for consistent experimental results (DOI: [10.1021/jacs.5b11918](https://doi.org/10.1021/jacs.5b11918)).

In the past few years, engineered self-assembly has begun to match the complexity of biological structures. The researchers suggest that future work should emphasize programmed design pathways that remain robust despite variation in experimental protocols. They also acknowledge that the optimization approach they describe has only been tested in a small number of simulation studies. Collaboration between theory and experiment, they say, is the key to drive further progress.

Jenny Morber, Ph.D.

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